EFFECT OF TEMPERATURE ON THE RAMAN SPECTRUM OF GLYCERINE *

By A. L. SUNDARA RAO, M.Sc.
Andhra University, Waltair

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ABSTRACT The Raman spectrum of Glycerine was photographed and it revealed 16 Raman lines. The frequencies of the lines are 419, 479, 549, 674, 820, 850, 919, 977, 1054, 1112, 1247, 1300, 1370, 1408, (?), 1463, 2889, 2949. A general assignment of frequencies as due to the C-C, C-O, C-H and δ(C-H) oscillations has been made. The effect of temperature on the Raman spectrum of Glycerine has been investigated. The line 674 becomes more diffuse at higher temperatures and increases in frequency by 20 cm^{-1} at 100°C. The 820 component accompanying the 850 line disappears at the higher temperature. These changes which are similar to those with solution in water are explained as due to depolymerisation of Glycerine complexes.

In the course of a general investigation of the Raman spectra of polybasic alcohols, glycerine was taken for examination. Among the various workers who have studied the Raman spectrum of this substance, mention must be made of Bar [1] and more recently Saxena [2]. The latter has studied the effect of dilution with water at two different concentrations and has observed that the 674 cm^{-1} line becomes more diffuse at higher dilutions and the intensity maximum is shifted by 15 cm^{-1}.

EXPERIMENTAL

In the present investigation the author has repeated the work of Saxena (*loc. cit.*) at the dilutions of 75% and 25% and verified his conclusions. It was thought desirable to see the effect of temperature on the Raman spectrum of glycerine with a view to understanding the cause of the changes with dilution and so the present work was undertaken.

The Wood's tube containing glycerine was placed inside a cylindrical electrical heater 5cm in diameter and 28cm long, open at either end. The heater was provided with a window 2 × 14cm long for allowing the incident radiation. The light from a mercury arc was focussed by a 9″ glass condenser on to the tube containing glycerine. A solution of sodium nitrite was placed between the condenser and the scattering medium. This served to eliminate the 4046 line of the mercury arc and to reduce to a marked extent the continuum lying between 4358 and 4916.

A two prism spectrograph of high light gathering power was used and an exposure of 10 hours was found sufficient to photograph the entire Raman

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spectrum. A comparison spectrum of copper was given on the same plate using a Hartman's diaphram and the wavelengths determined by measuring on a Hilger comparator.

RESULTS

The results of the investigation are given in Table I, along with the frequencies reported by Bar and Saxena for purposes of comparison The assignment of frequencies to the respective valence bonds are given in Column IV of the Table.

Many of the new frequencies reported by Saxena could not be confirmed by the author, inspite of the clear spectra that were obtained. It is surprising that no trace of the OH band could be found by the author in the case of glycerine even after prolonged exposure for 50 hours.

Effect of Dilution and Temperature

The effect of hydrogen bond formation is to create polymers in a liquid and the greater the number of hydroxyl groups present in a molecule the larger is the size of the polymer formed and the greater the degree of association

On dilution, the association breaks down and as a result some frequencies might be expected to get weakened or modified. In acetic acid, Leitmann and Ukholin[3] and Koteswaram[4] have observed that the 620 line diminishes in intensity with dilution and Koteswaram further reports that the 872 line also disappears at higher temperatures.

In glycerine the lines 604, and the 820 component accompanying the 850 line show a similar behaviour. The 674 line gets weaker and diffuse on dilution and the frequency increases by 20 cm^{-1}. The increase of temperature from 30° to 100°C has a similar effect. The feeble line of Raman frequency 820 either disappears or becomes too feeble to be perceptible in the spectrum of glycerine taken at 100°C.

Koteswaram (*loc. cit.*) in his work with acetic acid pointed out that the Raman line at 1700 corresponding to the C=O oscillation increases in frequency with dilution and with increased temperature. He explained this as due to the depolymerisation of the acid When one molecule is associated with another, the valency bond between atoms in any group within the molecule or that between two groups in the molecule are likely to be weakened. Thus the Raman frequency corresponding to any oscillation in an associated molecule, particularly the oscillation of a bond nearest to the associated molecule or molecules, should be smaller in the associated state than in the depolymerised one. The 674 line in glycerine must be due to an external oscillation in its molecule. In the pure state and at lower temperatures, there is possibly association. In solutions in water and at higher temperatures, there is depolymerisation, on account of which this external bond between two groups (it is difficult to definitely assert to which pair of groups this oscillation corresponds) is

strengthened with a consequent increase in the corresponding Raman frequency. The increased diffuseness of this line with dilution or with increase of temperature indicates that there may be superposition of two lines—one corresponding to the associated molecules in the pure liquid at the lower temperature and the other due to the depolymerised molecules in solution or at higher temperatures.

The feeble 820 line may be due to the C-C oscillations of the associated molecules and therefore naturally disappears at higher temperatures or in solutions as these molecules giving rise to this line are depolymerised.

TABLE I

Raman Frequencies of Glycerine

Bar (1933)	Saxena (1939)	Author	Assignment and Remarks
	328(1)		
	370½)		
427	419(3) br	419(3) br	
	434(½) s		
497	486(0) br.	479(5) br.	
553	540(1)	540(1)	
684	674(2)	671(2)	Becomes more diffuse at higher dil and at higher temperatures
822	817(3) s	820(3) s	Disappears at higher temperatures
850	847(6)	850(6)	C-C
	862(2) s		
919	919(2) br	919(5)	
977	975(2) s	977(2)	
1055	1048(8) br	1054 8) v br	C-O
	1085(2)		
1108	1112(5) s	1112(7) v br.	
	1104(1)		
1242	1246(2) v br	1247(3) br	
	1309(1) s	1300	A broad band extending over 100 cm⁻¹ containing three maxima
	1378(0)	1370	
		1408	
1471	1466(8) s	1463(10) s	δ(C-H)
2888	2886(12) br.	2889(12) br	Valence (C-H)
2947	2955(12) v br	2940(12) v br	

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4 Koteswaram. *Zeits. f. Physik* , **110**, 118, 1938